Mechanism of Enhanced Impact Strength of Poly(vinyl chloride) Modified by Acrylic Graft Copolymer

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SYNOPSIS

The mechanism of enhanced PVC impact strength of poly(vinyl chloride) modified by an acrylic graft copolymer was studied by the three-point bending test on a U-notched bar. *In the mechanism, the void formation from the modifier released the constrained strain.* The release suppresses the stress below the fibril strength in the material; consequently, stable deformation can develop over a large area and, thus, the impact strength of PVC modified by the acrylic graft copolymer is improved. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It has been well known that the enhanced impact strength of polymer alloys is attributed to the absorption of energy due to plastic deformation caused by shearing and crazing.[1-3] For the case when a modifier is dispersed in a brittle polymer matrix, the absorption mechanism of energy caused by plastic deformation in the polymer alloy has been discussed from various viewpoints. For example, Wu[4,5] suggested that shearing deformation is dominant when the distance between the interfaces of the modifier particles is less than a certain value.

The impact strength of the polymer is generally evaluated by the Izod impact test. In this test, the velocity of deformation is not constant and the process of deformation and fracture is complex. Therefore, these factors make the analysis of the result difficult. Based on the experimental result of the three-point bending test with a constant loading rate using a U-notched specimen, in which the testing process of deformation and fracture is simple, it is suggested that brittle fracture of a polymer occurs when the concentrated stress due to constrained plasticity overcomes the fibril strength of the material.[6,7]

Under the condition in which a fracture occurs in such a mechanism as mentioned above, there are two ways to improve the toughness, i.e., improvement of the fibril strength and suppression of the concentrated stress due to constrained plasticity below the fibril strength. A mechanism is proposed for describing the improved toughness of polymer alloys, in which voids developed at a modifier or crazes initiated from the voids due to stress concentration release the constrained strain. The mechanism makes the concentrated stress relaxed to stabilize the deformation and to suppress the stress below the breaking strength; thus, fracture is prevented. The validity of such a mechanism for the toughening of a polymer alloy has already been discussed for polycarbonate (PC) blended with a poly(acrylonitrile–butadiene–stylene) (ABS) copolymer.[8,9] It is suggested from this mechanism that the toughness of polymer alloys may depend on the density of the voids, which is controlled by both the number and strength of the modifier.

The purpose of this study was to analyze the mechanism of enhanced impact strength of PVC modified by an acrylic graft copolymer based on the fracture mechanism in terms of constrained plasticity of polymer material.

EXPERIMENTS

Preparation of Acrylic Graft Copolymers

A mixture of *n*-butyl acrylate and allyl methacrylate was copolymerized by conventional emulsion polymerization to obtain acrylic rubber latex; then,

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methyl methacrylate was graft-copolymerized to obtain the acrylic graft copolymer. The acrylic graft copolymer was cut using a microtome to obtain an ultrathin specimen. The specimen was observed using a transmission electron microscope, Model JEM 100CX Nippon Denshi, to determine the number-average particle diameter. By varying the amount of emulsifier for acrylic rubber polymerization, acrylic graft copolymers with different particle diameters were prepared. The measured particle diameter is shown in Table I.

Preparation of PVC Resin Compound Specimens

PVC compound contained 100 parts by weight of PVC resin with a degree of polymerization of 700, 3.5 parts by weight of dibutyltin maleate, 0.8 part by weight of polyhydric alcohol, and 0.4 part by weight of an acrylic process aid. The PVC resin compound was mixed with a prescribed amount of the modifier and extruded using a single-screw extruder with a diameter of 25 mm to make a square bar with a size of 6.35 × 12.7 mm and a sheet with a thickness of 0.5 mm.

Evaluation of Mechanical Properties

The dependence of yield stress on addition of the modifier was evaluated by measuring the uniaxial tensile strength using a Shimazu Autograph DSS-5000 under a strain rate of 0.1/min on specimens with a width of 6 mm and a length of 150 mm which is cut from the extruded sheet with a thickness of 0.5 mm. The dependence of yield stress on strain rate was evaluated using a Shimazu Servopulser on the same specimen as mentioned above over a strain rate range of 0.03125–3.125/s.

The dependence of toughness on addition of the modifier was evaluated by measuring the three-point bending test on a U-notched specimen with a ligament of 3 mm, radius of notched tip of 0.5 mm, and the span length of 40 mm as shown in Figure 1. For brittle samples, the bending rate of 2 mm/min was employed, and the dependence of toughness on the bending rate was examined at a range of 0.125–125

Table I Diameter of Particle and Elstic Modulus in Modifier

Modifier	Diameter of Particle (μm)	Elastic Modulus (MPa)
Modifier(A)	0.188	10.8
Modifier(B)	0.148	10.8
Modifier(C)	0.074	10.8

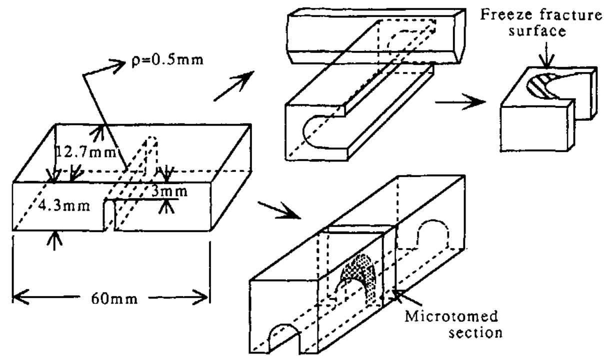

Figure 1 Dimensions of the U-notched sample and cutting direction for observation of the deformation.

mm/s. The impact strength was measured by an Izod impact test using a V-notched specimen in accordance with ASTM D 256.

Analysis of Deformation Process

To discuss the deformation processes of U-notched bars in the three-point bending test under plane strain, thin sections of about 25 μm were cut normal to the plane of the initial notch using a microtome as illustrated in Figure 1. The morphology of the craze and plastic deformation zone was studied with an optical microscope for the microtomed sections. The changes in microstructure were observed with a scanning electron microscope for the surfaces of cryogenically fractured samples. Samples, which were subjected to the bending test, were first immersed in a liquid nitrogen bath for 5 min and then broken to the plane of the notch immediately after removal. Because strain recovery on unloading influences significantly the morphology of the deformation zone, the deformation by three-point bending was fixed by the casting of epoxy resin, which consisted of 100 parts per hundred of resin (phr) of

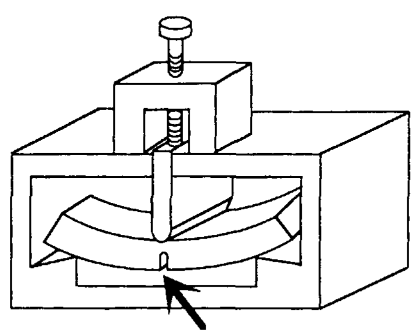

Figure 2 Fixation of strain by casting with an epoxy resin.

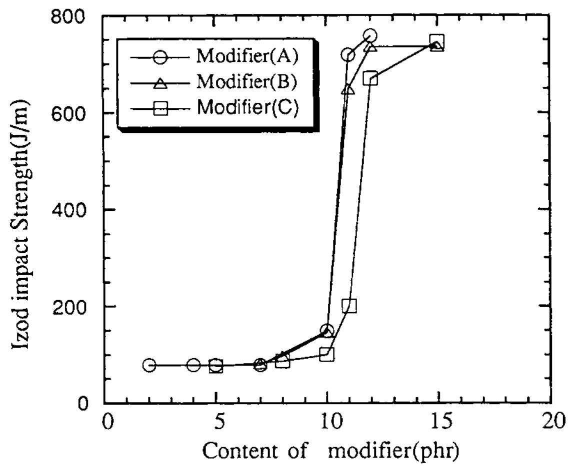

Figure 3 Effect of the amount of modifier on the Izod impact strength.

Epon 828 and 60 phr of Ankamide 506, as shown in Figure 2.

RESULTS

Impact Strength and Toughness

The enhanced effect on impact strength of PVC by addition of the modifier is shown in Figure 3, wherein modifiers with three different dispersed particle diameters were used. The impact strength increases greatly at the addition of 10 parts by weight of the modifier without depending on the particle diameter of the modifier. Because the speed of the pendulum of an Izod impact tester changes after impacting on a specimen, the mechanism of deformation and fracture is complex. Figure 4 shows the variation of toughness with increase of the content of modifier in the three-point bending test on U-notched specimens. The result is naturally dependent on the bending rate. For the bending rate of as low as 2 mm/min [Fig. 4(a)], the mode of deformation changes from brittle fracture to ductile deformation, showing a general yielding by addition of only 1 part by weight of the modifier. On the other hand, for a bending rate as high as 125 mm/s [Fig. 4(b)], as much as 10 parts by weight of the modifier is required for the mode of deformation to change to ductile deformation. The toughness evaluated in the three-point bending test was also independent of the particle diameter of the modifier in the same manner as was the impact strength. The modifier content required to change the deformation from brittle to ductile in the high-rate deformation test approximately coincides with that required it improve the impact strength in the Izod impact test. In the Izod impact test, the speed of a pendulum is about 3 m/s at the position just before impacting against the specimen. The speed is one order faster than that in the high-speed three-point bending testing. In Izod impact testing, the speed of a pendulum is the repeated load. Therefore, the actual average speed of deformation exerted on the specimen is slower than that just before impact. The result of this experiment suggests that the bending speed of 125 mm/s is equivalent to the average speed in the Izod impact test.

Yield Stress

The stress generated at the tip of notch in the ductile material is sensitive to the yield stress because the mechanism of stress concentration involves a constraint of plasticity.[6,10] Figure 5 shows the change in yield stress with varying the added amount of

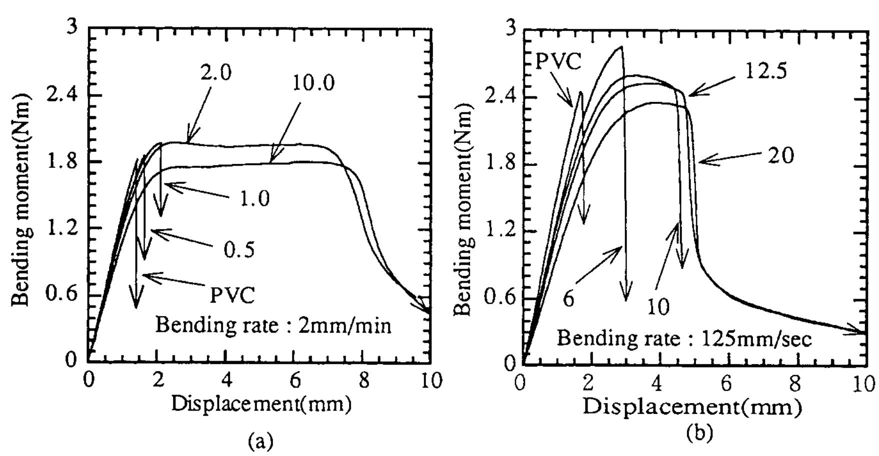

Figure 4 Variation of the bending moment-displacement curves as a function of the content of modifier.

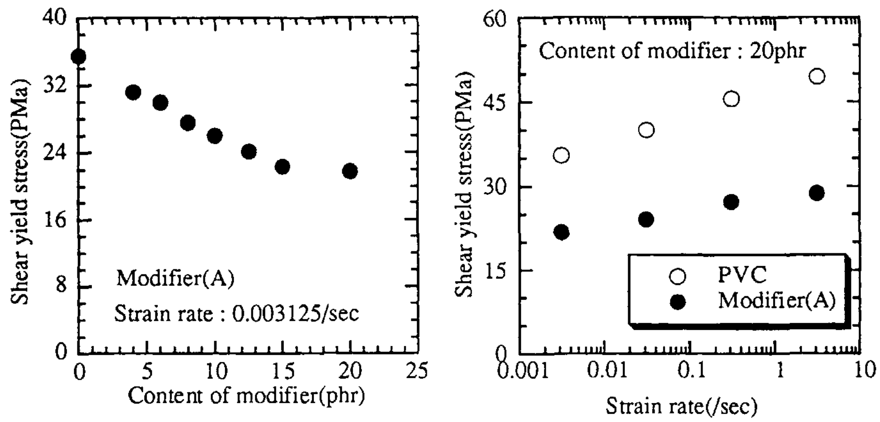

Figure 5 Shear yield stress of toughened PVC.

modifier and the strain rate. In this experiment, samples with the modifier [Modifier (A)] added with the largest particle diameters were used. The variation of yield stress with strain rate was examined on the samples with 20 parts by weight of the modifier added. Because of low rigidity of the modifier, naturally, the yield stress decreases with increase of modifier content, i.e., the addition of the modifier facilitates the plastic behavior. Since the increase in strain rate causes the increase in yield stress, plastic deformation in high-speed loading naturally causes an increase of stress concentration at the tip of local plastic zone developed from the notch tip.

Shape and Fracture in Plastic Deformation

Figure 6 shows a micrograph of local plastic zone on which fanwise shear bands are formed at the tip of notch in PVC and a scanning electron micrograph of crazes formed at the tip of the plastic zone. The bending rate was 2 mm/min. The formation of the plastic zone causes stress concentration at the tip of the zone due to plastic constraint. Stress is maximum at the tip of the plastic zone. The maximum stress increases with development of the plastic zone, and when it reaches a certain critical value, crazes, which are unstable, and local deformation develop. Brittle fracture occurs when fibrils, which constitute crazes, are broken to form a crack. The area of the plastic zone develops with increase of the applied load. The developed size of the plastic zone at the time when crazes appear decreases synchronously with the toughness as the bending rate increases. Figure 7 shows the deformation process of the polymer alloy comprising brittle PVC and 4 parts by weight of the acrylic graft copolymer. The bending rate was as relatively high as 12.5 mm/s. Initially, plastic deformation begins with formation of shear bands at the tip of the notch in the same way as in the case of PVC. When the plastic zone develops to a certain size with increasing displacement, formation of voids occurs from the modifier as shown in the scanning electron micrograph of Figure 8. Although the micrograph in Figure 8 is not convining for showing void formation due to deformation, because the fallout of undeformed particles by cryogenetic fracture may create the void fracture on the fracture surface, formation of the void was speculated from the diffusion of the immersion liquid (liquid parafinn) into voids, which clarifies the cross section on the optical microscopic observation. Further increase of the applied load causes a large development of the plastic zone containing voids. When the displacement exceeds 2.5 mm, the plastic deformation at the tip of plastic zone becomes unstable, causing local concentration of the strain, and a crack is formed at the concentrated point to trigger the fracture.

Figure 9 shows the fracture surface of a specimen fractured as mentioned above. There is a fracture nucleus showing the initiation of fracture at the point distant from the tip of the notch. The relationship between the distance from the tip of the notch to the fracture nucleus and the content of the modifier is shown in Figure 10 together with the Izod impact strength. The bending rate was as high as 125 mm/s. The distance corresponds to the size of the plastic zone which had developed until a crack began to form at the tip of notch. It is obvious that the size of the plastic zone which had developed until a crack began to form increases with increase of modifier content. In the case of samples containing the modifier in an amount exceeding 10 parts by weight, the plastic zone initiated at the notch develops to the opposite side of the specimen, namely, general yielding; therefore, the fracture does not initiate from the inside but the specimen deforms in a ductile manner. The modifier content at which

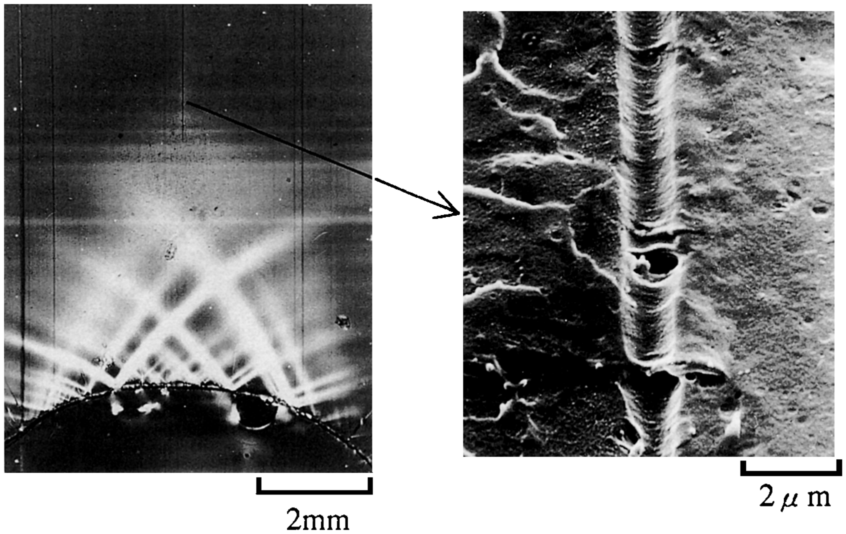

Figure 6 Micrographs of local plastic deformation zone and craze of PVC.

the behavior of the plastic zone changes to a general yield in the high-rate bending test of the U-notched specimen is naturally equivalent to that at which the impact strength is improved in impact testing.

DISCUSSION

In general, from a microscopic viewpoint, the polymer has a heterogeneous structure and has distributed cohesive strength. When a load is applied on such a material, the microscopic fracture occurs at the point where cohesion strength is weak to form a microvoid. The increase of applied load causes the increase in the number of voids, and a further increase of the load causes the expansion of the voids with circumferential plastic deformation of the voids. In this case, when transferring the speed of the elastic strain energy stored in the material for expanding the voids is greater than that of the plastic deformation energy required to expand the voids, in the mechanism similar to the brittle crack transmission theory by Griffith,[11] the void meet with a plastic unstable condition and expand rapidly. This is the mechanism of craze formation in

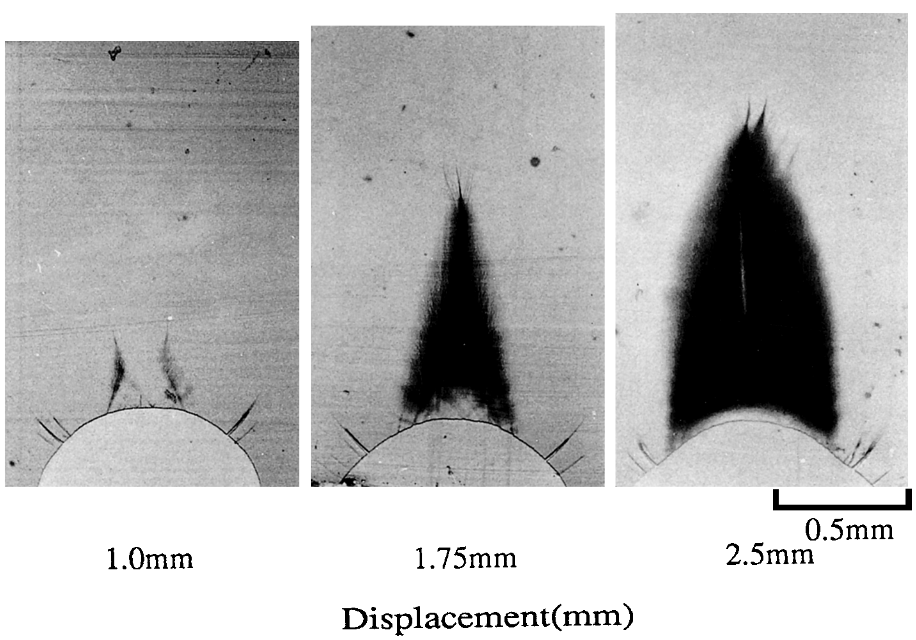

Figure 7 Deformation process of PVC blended with 4 php of modifier (A).

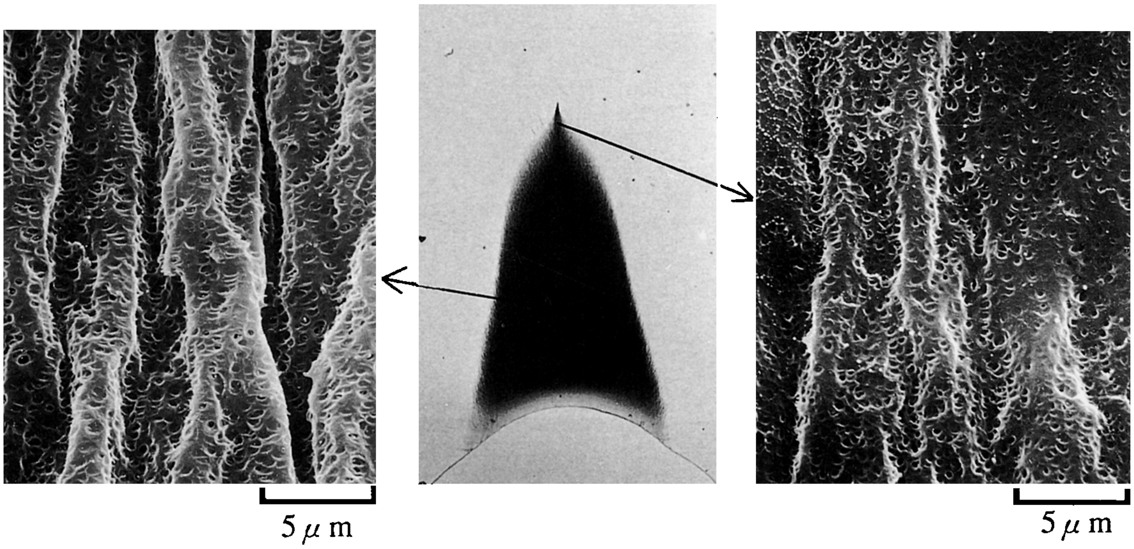

Figure 8 Scanning electron micrographs of the microcraze of PVC samples blended with 8 php of modifier. Deformation rate; 125 mm/sec.

a polymer.[12] When stress exerted on crazes comprising oriented fibrils exceeds the strength of the fibrils, cracks are formed and brittle fracture occurs. The formation of craze depends on various conditions such as temperature, strain rate, and structure of the polymer. The craze-forming stress of PVC deformed at a strain rate of 125 mm/s is calculated to be 102 MPa according to the elastic–plastic theory based on the yield stress and the position of the fracture nucleus shown in Figure 10.[6,7,10]

Assuming that PVC is fractured in the mechanism as described above, the improvement of fibril strength of PVC or suppression of the maximum stress below the fibril strength are considered to be the methods for controlling the fracture. For improvement of the fibril strength of the craze, the increase of molecular weight is effective[8,13]; however, increased molecular weight is disadvantageous for molding. It is well known that the constraint of strain, which prevents Poisson shrinkage, causes stress concentration on a notch. In the case of material containing an elastomer with reduced cohesion as the modifier, the increase of applied load causes the formation of the void preferentially. The breeding of the void proceeds to a sufficient densely crowded condition and Poisson shrinkage occurs between voids. Under such a condition, the strain is released from restriction to reduce the stress concentration.[8] The breeding of voids in the plastic zone of PVC modified with the acrylic graft copolymer

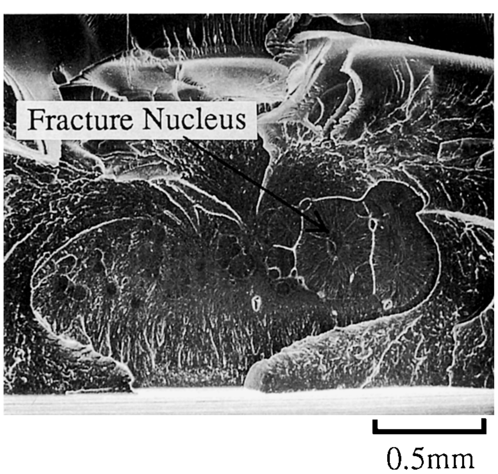

Figure 9 Scanning electron micrographs of the fracture surface of PVC blended with 4 php modifier.

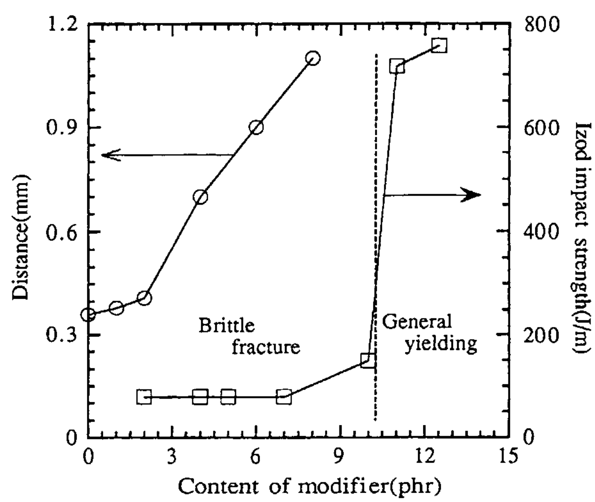

Figure 10 Relationship between Izod impact strength and the distance from the notch tip to the fracture nucleus of toughened PVC.

are observed in the micrograph of Figure 7 and the scanning electron micrograph of Figure 8. Generally, it is considered that a void forms at the interface of a modifier, but in the case of the acrylic graft copolymer, the evidence of the void formation at the interface was not confirmed.

As examined above, the craze-forming stress of PVC is 102 MPa. The addition of the acrylic graft copolymer, the strength of which is smaller than 102 MPa, likely causes the decrease of the craze strength of the modified PVC. The fact that the size of the plastic zone at the fracture shown in Figure 10 increases with increasing of modifier content suggests that the release of constrained strain due to void formation compensates sufficiently the decrease in craze strength of the modified PVC.

In addition, a low elastic modulus of the acrylic graft copolymer leads to a decrease in yield stress of the modified PVC, as shown in Figure 5, and the improvement of toughness due to the relaxation of stress concentration was supplemented by the plastication effect.

CONCLUSION

The improvement mechanism of the impact strength of PVC by addition of an acrylic graft copolymer was analyzed based on experimental results of the three-point bending test on U-notched specimens. This test method was employed because the fracture process in the test is simple and favorable for easy analysis. In the mechanism, the void formation from the modifier releases the constrained strain; the release suppresses the stress in the material below the fibril strength. Consequently, stable plastic deformation can develop over a large area; thus, the impact strength is improved.

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